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CHEMICAL COAGULATION DOSAGE CONTROL.(U)

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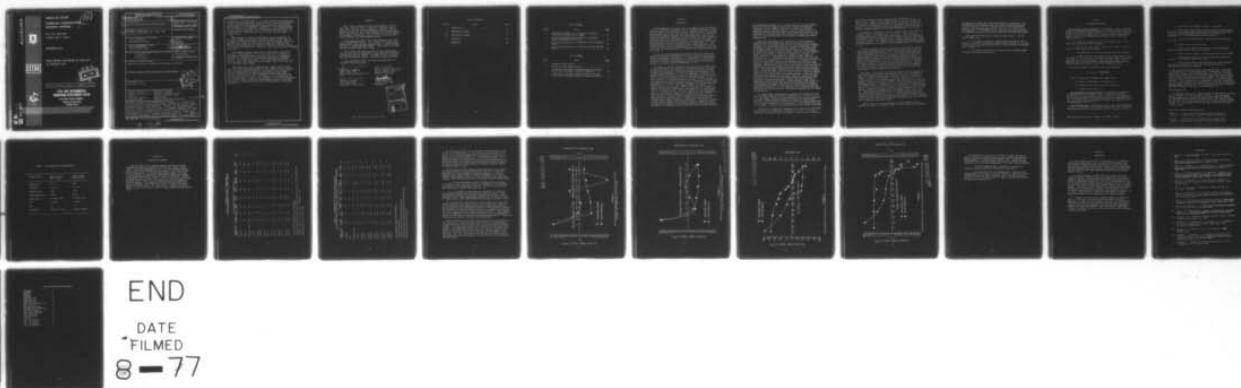
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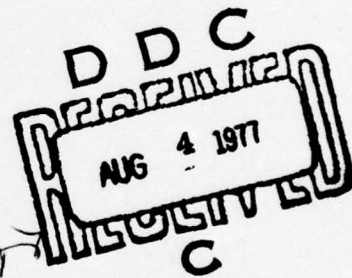
**CHEMICAL COAGULATION
DOSAGE CONTROL**

DET 1 HQ. ADTC/ECW

TYNDALL AFB, FL. 32403

DECEMBER 1976

FINAL REPORT FOR PERIOD 30 JUNE 1973
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**CIVIL AND ENVIRONMENTAL
ENGINEERING DEVELOPMENT OFFICE**

(AIR FORCE SYSTEMS COMMAND)

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FLORIDA 32403

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <p>Quality control in the potable water industry is a subject that is receiving much attention with the current concern over organic contamination of water supplies. However, if one ponders the routine methods of quality control, it becomes apparent that even the more classic contaminants are estimated by indicators. More specifically, our entire quality control program, at most water treatment facilities, is based upon three analyses: (1) turbidity, (2) chlorine residual, and (3) coliform count. Of these three</p>												

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indicators, coliform count is an after-the-fact documentation of poor quality; chlorine residual is an indicator of bacteriological quality with reasonably good empirical correlation; and turbidity is an aesthetic parameter. Some would suggest that turbidity is a powerful indicator of both aesthetic and potable quality; however, the literature indicates that the foundations of these criteria are so vague as to suggest nonexistence.

The purpose of this investigation was to determine if the best dosage for various coagulants would be the same if a number of indicators were used as the best dosage criteria. Specifically, what is the indicated best coagulant dosage between zeta potential, colloidal titration, apparent color, true color, COD reduction, turbidity reduction, and bacteriophage reduction.

Two types of water were used to empirically determine the above relationships. The first water was a secondary wastewater treatment plant effluent; the type of wastewater that may be delivered to an advanced wastewater treatment system. The other water was a relatively unpolluted raw surface water; the type of surface supply that is often used for a potable water supply.

The results of this investigation, after testing with nine different coagulant/coagulant aid combinations, revealed that the best dosage varies as a function of the indicator used to determine that dosage. The assumption by some previous investigators that a parallel relationship exists between many of these tests was shown to be inaccurate for the waters tested. Lastly, the results of this study indicate that a great deal of new and imaginative research is needed to establish an acceptable quality control base in the water industry.

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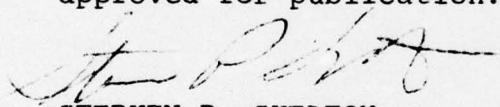
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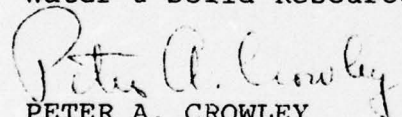
This report summarizes work done between 30 June 1973 and 1 January 1976. Stephen P. Shelton, Capt, USAF, BSC, was the project engineer; however, the laboratory portion of the investigation was accomplished while Capt Shelton was a PhD candidate at the University of Tennessee, Knoxville, as part of a University sponsored research and development project.

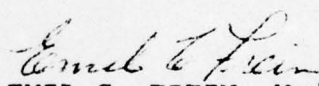
This technical effort was done under the Air Force Civil Engineering Center. On 8 April 1977 AFCEC was reorganized, creating two organizations - AFCEC (AFESA) and Det 1 (CEEDO) HQ ADTC (AFSC). This effort was completed and published under CEEDO.

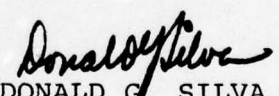
This report has been reviewed by the Information Office (OI) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.


STEPHEN P. SHELTON
Capt, USAF, BSC
Water & Solid Resource Div


PETER A. CROWLEY
Maj, USAF, BSC
Director of Environics


EMIL C. FREIN, Maj, USAF
Chief, Water & Solid
Resource Division


DONALD G. SILVA
Lt Col, USAF, BSC
Commander

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TABLE OF CONTENTS

Section	Title	Page
I	INTRODUCTION	1
II	EXPERIMENTAL METHODS	4
III	DISCUSSION OF RESULTS	9
IV	CONCLUSION	18
	REFERENCES	19

LIST OF FIGURES

Figure	Title	Page
1	Electrophoretic Mobility as a Function of Aluminum Sulfate and Coagulant Aid 253 Dosage	13
2	Electrophoretic Mobility as a Function of Aluminum Sulfate and Magnifloc 860 Dosage	14
3	Electrophoretic Mobility as a Function of Ferric Sulfate Dosage	15
4	Electrophoretic Mobility as a Function of Ferric Chloride Dosage	16

LIST OF TABLES

Table	Title	Page
1	Wastewater Characteristics	7
2	Raw Surface Water Characteristics	8
3	A Comparison of the Best Coagulant Dosage for the Wastewater Tested With Respect to Various Indicators	10
4	A Comparison of the Best Coagulant Dosage for the Raw Surface Water Tested With Respect to Various Indicators	11

SECTION I

INTRODUCTION

From the examination of Stoke's law, it is apparent that the settling velocity of particles suspended in water is directly proportional to their size and density. Some of these particles, colloids because of their size and/or density, would remain in suspension indefinitely due to the balance between their settling properties and stabilizing forces, specifically electrical dispersion, solvation by water molecules, and physical-hydraulic characteristics of the sedimentation basin. Colloids are very small particles ($<1\mu\text{m}$) (Reference 5); because of their small size and negligible weight they have poor settling characteristics (References 2, 7). Colloidal behavior in water is controlled by the surface properties of the colloid; in order to effect a destabilization of the suspension, one first must modify the surface properties to stimulate agglomeration (References 5, 11, 21).

In order to facilitate separation from the bulk of the liquid flow stream by conventional sedimentation practices, these particles must be forced to agglomerate (References 2, 7). Agglomeration is accomplished by decreasing and/or eliminating the previously mentioned stabilizing forces to a level where the Brownian motion and Van der Waals forces of attraction can become dominant (References 2, 3, 27).

The process of chemical coagulation and flocculation has great application in the removal of dissolved and colloidal substances from water. In previous years two basic theories of coagulation have been advanced to express the mechanisms of colloidal stability and coagulation. The physical theory (References 3, 7, 19, 26) emphasizes the concept of the electrical layer and the significance of predominantly physical factors, such as counter-ion adsorption, reduction of zeta potential, and ion pair formation in the destabilization of colloids. The interpretation of the physical theory has been furthered by the interpretation of flocculation effects by an exact mathematical treatment of the double-layer model (References 3, 7, 11, 26). The surface chemistry of colloids is, in itself, a subfield of chemistry; therefore, this paper will attempt to explore only the basic considerations with respect to the surface properties of colloidal material. Colloidal material may be subclassified into two categories with respect to its affinity for water (Reference 11). Most organic colloidal materials have surface active groups such as hydroxyl (OH^-) or carboxyl (COOH^-) (Reference 26); these groups attract water molecules (water molecules are polar) and form a water-bound envelope; hence, organic colloids are hydrophilic. Conversely, inorganic colloids do not normally have functional groups in a manner to attract the polar water molecule; their electrical properties are controlled by preferential ion adsorption from the solution; hence, inorganic colloids

are hydrophobic (References 6, 14). Most naturally occurring colloids have a net negative charge (Zeta Potential) in the normal pH range (References 14, 25); however, some clays or industrial wastewater components may have a positive charge. A specific example would be an industrial operation that discharges large quantities of proteins. This would lead to a situation where the colloids would demonstrate negative charge at low pH and positive colloidal charge at moderate and high pH (Reference 25).

Parakinetic coagulation is the term used to describe colloidal instability caused by modification of the colloid's surface chemistry (Reference 14). The primary consideration in colloidal surface chemistry is charge; the specific charge that is of paramount importance to the Environmental Engineer is the net shear charge; i.e., Zeta Potential. To be properly used, Zeta Potential must be visualized. The following discussion will attempt to create a visual concept of what Zeta Potential is and its relationship to the surface chemistry of a colloid. The actual charge on a colloid particle is called the Nerst Potential (References 10, 11). Surrounding the colloid is a layer of counter-ions which effectively become a part of the colloid. This counter-ion layer is called the Stern layer, and its associated charge is called the Stern Potential. Beyond the Stern layer is a diffuse layer of counter-ions, sometimes called the Gouy layer, that are not tightly bound to the colloid. Beyond the Gouy layer is the bulk solution in which the colloid is suspended. The surface which separates the Stern layer from the Gouy layer forms a surface for shear. Zeta Potential is the electrostatic potential required to overcome the shear force on this surface. Since like charges repel, effective agglomeration of colloidal material is difficult until this shear (Zeta Potential) is near zero. When this occurs, the destabilization forces in the colloidal suspension may become dominant and orthokinetic coagulation may begin. Simply, physical theory can be summarized by the idea that foreign ions are adsorbed on the surface of dispersed particles; hence, these particles are electrically charged. When coagulants are added, flocculation is brought about by counter-ion adsorption (References 2, 10) and compaction of the diffuse part of the double layers. The process can be visualized by assuming that the charges are neutralized.

The second theory, Chemical Theory, assumes that colloids are aggregates of defined chemical structure (References 2, 4, 7, 10, 18, 19, 25, 27). The primary charge on a colloid particle arises from the ionization of complex inorganic groups present on the surface of the dispersed particles. Destabilization of colloids is caused by chemical interactions such as complex formation and proton transfer or, more specifically, loss of a hydrogen ion and gain of an organic group with the metallic hydroxide.

The physical or double-layer theory has been developed in great detail and has gained wide acceptance (References 19, 26, 29). It has been developed to the point of being an effective research tool in coagulation

work and has virtually replaced chemical theory (References 3, 20). A point to note, however, is that these theories are not mutually exclusive (Reference 6). Research has indicated that purely chemical factors must be considered in addition to the theory of the double-layer in order to explain, in a more quantitative way, the dependence of colloidal stability upon the chemical composition of the medium (References 5, 19, 23, 30).

A coagulant is a chemical or group of chemicals which, when added to a solution, effects a destabilization of the surface properties of the colloidal material and thereby permit flocculation. The effectiveness of the parakinetic portion of this process is related directly to the valence of the ionic form of the coagulant. Higher valences normally yield a more efficient coagulant. This relationship is of substantial importance because the effectiveness, due to valence, is approximately exponential (References 5, 11).

In some high quality raw waters, the use of a coagulant with an oppositely charged coagulant aid will sometimes facilitate a more effective coagulation process (References 5, 13). This occurs because these oppositely charged materials will form a "seed" microfloc from which orthokinetic coagulation may proceed. Orthokinetic coagulation refers to agglomeration by collision of "sticky" particles and/or the "brush pile" effect caused by polymers. This is the primary mechanism that operates between the formation of the microfloc and the settling of the macrofloc. Two common coagulant aids used are sodium-aluminate and clay. Polymers are also used in this reverse-seed process and may yield an advantage over sodium aluminate or clay in their ability to form long chain-like structures that improve orthokinetic coagulation.

When water is coagulated, two discrete types of colloids are present, those present in the natural water and those found by the coagulants; a number of in-between colloids which represent a mixture of natural and chemical colloids are also present. Colloidal charge may be caused by ion adsorption from the suspending waters (References 8, 9, 10, 12, 17); however, in most cases of water treatment, with the exception of industrial wastewater treatment (References 9, 26), the most substantial portion of the colloidal charge is produced by direct ionization of colloidal constituents. The functional groups, contained by the colloids, are normally the hydroxyl, carboxylic, phosphate, and sulfo groups (References 22, 25, 26, 27). These groups form complexes with polyvalent metallic ions. This fact suggests the possibility of specific chemical penetration between colloidal material and metallic ions. It therefore seems logical to consider the possibility that the destabilization effect of certain ions might be more accurately determined by chemical interaction than by the exclusive use of counter-ion adsorption theory.

Without regard to the exact mechanism of floc formation, better methods for control of coagulant dosage for water and wastewater treatment

are necessary to insure the health and welfare of the population. The "standard" jar test procedure along with standard laboratory analyses, such as turbidity, color, etc., has been and is now the most popular means for controlling coagulant dosage. Location of the point of zero electrophoresis or Zeta Potential as an additional operational parameter for coagulant dosage control has gained favor over the past several years.

This paper is concerned with coagulant dosage control; it has two specific objectives:

1. To compare a relatively unused method of isoelectric point location of titration, developed by Kawamura (References 14, 15, 16) with the now relatively standard electrophoretic mobility method for isoelectric point location, and
2. To compare both methods with observed best coagulant dosages for physical and bacteriophage tests.

SECTION II
EXPERIMENTAL METHODS

The Colloidal Titration Technique - The colloidal titration technique assumes that oppositely charged colloids will react stoichiometrically to neutralize the charge (References 14, 15, 16). A known amount of positive colloid is added to the sample, and the mixture is back titrated using a negative colloid. The colloidal titration method used is as follows (References 23, 30):

1. Add 100 ml of sample to a 250 ml Erlenmeyer flask. A distilled water blank should also be prepared.
2. Add 5 ml of 0.001 N methyl glycol chitosan (MGC), a positive colloid, to the contents of the flask.
3. Add three drops of 0.1 percent toluidine blue (TB) indicator.
4. Titrate with 0.001 N polyvinyl alcohol sulfate K(PVSK) using a microburet. The end point is indicated by a rather subtle color change from light blue to a bluish-purple. Since the color change is time dependent, the titration should be accomplished with all due haste and requires consistent titration times for all samples and blanks.

The colloidal charge is calculated from the relationship:

$$cc \text{ (meq/l)} = \frac{(A-B)N(1000)}{V}$$

where A = volume of PVSK added to the sample in ml,

B = volume of PVSK added to the blank in ml,

N = normality of the PVSK solution (0.001N), and

V = volume of the sample in ml.

The Electrophoretic Mobility Method - The Zeta-Meter, manufactured by Zeta-Meter, Inc. of New York was used to measure the colloidal adsorption of ions and/or polymers, which in effect allowed measurement of the colloidal charge (the electrophoretic mobility) (References 20, 21, 31). All Zeta potential measurements were made in accordance with the Zeta Meter Manual (Reference 31).

The Coagulation Test - All coagulation tests were simple, batch-type jar tests. A six-bladed stirring apparatus^a was used. The standard jar-test procedures used in this test were as follows (References 23, 30):

^aManufactured by Phipps-Bird Company of Richmond, Virginia

1. Add 1000 ml of the sample to each of six beakers.
2. While stirring at 100 rpm using the stirring apparatus, add sufficient bacteriophage stock solution (f2 bacteriophage) to each beaker to give an initial bacteriophage concentration in the beakers of approximately 1×10^6 plaque-forming units/ml (PFU/ml).
3. Quickly add coagulants and/or coagulant aids while stirring at 100 rpm.
4. Flash mix for 1 min at 100 rpm.
5. Pipet a 50 ml sample from each beaker for electrophoretic mobility measurement while stirring at 100 rpm.
6. Reduce stirring speed to 25 rpm and flocculate for 29 minutes.
7. Remove beakers from under stirring mechanism and allow the contents of the beakers to settle for 30 min.
8. Siphon the top 500 ml from each beaker for further analysis. Care should be taken not to siphon any floc that may float or be disturbed on the bottom of the beaker.

The supernatant from each beaker, including the blank, was analyzed. The supernatant tests included measurements of temperature, turbidity, conductivity, apparent and centrifuged color, pH, alkalinity (as CaCO_3), chemical oxygen demand (COD), bacteriophage concentration, and colloidal charge by both of the previously discussed methods. The blank was used for percent reduction calculation for COD, turbidity, and bacteriophage removals. The pH, suspended solids, temperature, turbidity, conductivity, COD, color, and alkalinity were measured using the procedure recommended in Standard Methods (Reference 24). The bacteriophage were grown and quantified using a procedure described by York (Reference 30).

THE COAGULANTS USED

The coagulants used in this study included aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3$; ferric chloride, FeCl_3 ; ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{nH}_2\text{O}$ and sodium aluminate, $\text{Na}_2\text{OAl}_2\text{O}_3$. The polyelectrolytes tested were one cationic^a, two nonionic^b, and two anionic^c, polyelectrolytes. The cationic polymer was used both as a primary coagulant and as a coagulant aid with aluminum sulfate. All other polyelectrolytes were used as coagulant aids with aluminum sulfate.

^aCat Floc, a product of the Calgon Corp.

^bNonionic 1: Coagulant Aid #233 a product of the Calgon Corp;
Nonionic 2: Magnifloc 971, a product of American Cyanamid Corp.

^cAnionic 1: Coagulant Aid #253, a product of the Calgon Corp;
Anionic 2: Magnifloc 860, a product of American Cyanamid Corp.

At least two jar tests were run with each coagulant. The first test covered a wide band of dosages and was intended to go well beyond the isoelectric point of the colloids. The second test was a more precise determination of the isoelectric point as well as of best coagulant dosage for other parameters:

Coagulant aids were investigated in two stages:

1. The aluminum sulfate was held constant while the aid was varied. In all cases, with the exception of the cationic polymer, the aluminum sulfate was held constant at the predetermined best coagulant dosage. With the cationic polymer, aluminum sulfate was held constant at 75-80 percent of the best coagulant dosage to encourage a more accurate measurement of the isoelectric point.

2. The aid was held at the apparent best dosage and the aluminum sulfate was varied downward from its unaided best dosage.

THE TEST WATERS USED

The test waters were diverse in order to effect a true difference in their characteristics. The first water was an unchlorinated effluent from Love's Creek wastewater treatment plant in Knoxville, Tennessee. The plant received primarily domestic wastewater and provides primary and secondary (trickling filter) treatment. Love's Creek treatment plant has a rather consistent effluent that varies in both flow and strength on a weekly cycle; hence, all samples were taken at the same time each week to effect the best possible correlation of data. All samples were of the grab variety and all tests were conducted within 18 hours after the samples were taken. Samples were refrigerated at 3°C between the time they were taken and testing; however, the test samples were permitted to come to room temperature (+20°C) before testing began. The average characteristics of the wastewater are shown in Table 1.

The second water was obtained at Davis Ferry, located at mile 5.8 (Tennessee Valley Authority Survey) on the Little Tennessee River in Loudon County, Tennessee. This water was chosen because it is representative of a rather unpolluted, raw surface water. The water was stored in two 55-gallon (208 liters) plastic drums shrouded in black paper to inhibit algae growth. Compressed air was supplied continuously at 10 psi (7.03 Kg/cm²) through 0.25-inch (0.635 cm) plastic tube to allow it to stabilize and to prevent settling. All tests were conducted as quickly as possible to promote consistency in results. The raw surface water characteristics are shown in Table 2.

TABLE 1. WASTEWATER CHARACTERISTICS

Characteristic	Average Value
Temperature when taken	14°C
Temperature when tested	22°C
Turbidity	3.9 JTU
Apparent color	19 SCU
Centrifuged color	10 SCU
Conductivity	475 μ mho at 25°C
COD	81 mg/l
pH	7.8
Alkalinity	188 mg/l as CaCO_3

TABLE 2. RAW SURFACE WATER CHARACTERISTICS

Characteristic	Before Testing Time: Days-0	After Testing Time: Days-12
Temperature	25°C	24°C
Turbidity	1.2 JTU	1.1 JTU
Apparent Color	5 SCU	5 SCU
Centrifuged color	0 SCU	0 SCU
Conductivity	64 μ mho at 25°C	67 μ mho at 25°C
COD	5.2 mg/l	5.4 mg/l
pH	7.5	6.5
Alkalinity	19 mg/l as CaCO_3	19 mg/l as CaCO_3

SECTION III

DISCUSSION OF RESULTS

A tabular resume of the coagulant dosages used for the various coagulants and waters as indicated by the tests are shown in Tables 3 and 4. From this comparison, it can be seen that coagulant dosage control must be further classified with respect to the indicator used for its determination. If overall potable water quality is desired, it may be possible to classify the best coagulant dosage with respect to the weighted average of a series of different indicators. However, it should be noted, in Tables 3 and 4, that in only four of the 18 cases presented did the dosage for virus removal agree with the dosage for turbidity removal. It is suggested therefore that this observation alone is substantial and creates doubt in the reliability of current methods for dosage control. More specifically, turbidity, the most widely used jar test indicator, does not always indicate the best quality water.

Table 3. A COMPARISON OF THE BEST COAGULANT DOSAGE
FOR THE WASTEWATER TESTED WITH RESPECT TO VARIOUS INDICATORS

Coagulant and/or Coagulant Aid	Colloidal Titration	Best Coagulant Dose (mg/l) as Indicated by:				Virus Removal	Average of All	pH ^a
		Zeta Potential	Apparent Color	True Color	COD Reduction			
Al ₂ (SO ₄) ₃	70	80	80	65	80	90	77.3	7.1
FeCl ₃	94	104	98	94	108	95	100.3	6.8
Fe ₂ (SO ₄) ₃ · nH ₂ O	200	128	162	170	150	194	168.6	6.5
Cationic	b	b	6.5	6.0	4.7	1.0 ^c	4.72	7.3
Al ₂ (SO ₄) ₃	60	50	55	50	65	50	56.4	7.3
Cationic	1.5	1.5	1.5	1.5	1.5	1.5	1.5	
Al ₂ (SO ₄) ₃	55	81	65	65	75	75	70.9	7.1
Nonionic 1	1.0 ^c	1.0	1.0	1.0	1.0	1.0	1.0	
Al ₂ (SO ₄) ₃	80	80	80	80	80	80	80	7.2
Anionic 1	0.43	0.20	0.50	0.50	0.80	1.00	0.576	
Al ₂ (SO ₄) ₃	d	75	40	40	60	65	59.2	7.2
Anionic 2	d	0.40	0.40	0.40	0.40	0.40	0.40	
Al ₂ (SO ₄) ₃	75 ^c , 64 ^c	80	50	50	80	70	68.6	6.7
Nonionic 2	0.50	0.20	0.50	0.50	0.60	0.50	0.463	

^apH of supernatant immediately after sedimentation.

^bIsoelectric point was not reached over the dosage range allowed by the U.S. Public Health Service.

^cTurbidity increased as dosage increased to a maximum of -44.0%.

^dMore than one isoelectric point observed.

TABLE 4. A COMPARISON OF THE BEST COAGULANT DOSAGE
FOR THE RAW SURFACE WATER TESTED WITH RESPECT TO VARIOUS INDICATORS

Coagulant and/or Coagulant Aid	Colloidal Titration	Zeta Potential	Best Coagulant Dose (mg/l) as Indicated by:				Average Removal of all	pH ^a
			Apparent Color	True Color	COD Reduction	Turbidity Reduction		
Al ₂ (SO ₄) ₃	14	12	10	b	20	15	15	6.8
FeCl ₃	32	37	25	b	48	34	40	6.8
Fe ₂ (SO ₄) ₃ · nH ₂ O	42	65	35	b	38	35	62	7.2
Cationic	1.5	c	d	b	0.51	0.56	2.2	7.5
Al ₂ (SO ₄) ₃	7.2	9.2	6.0	b	8	8	8	6.8
Cationic	0.25	0.25	0.25	b	2.25	0.25	0.25	0.583
Al ₂ (SO ₄) ₃	9	7.0	6	b	10	10	10	6.8
Nonionic 1	.25	0.25	0.25	b	0.50	0.25	0.25	0.458
Al ₂ (SO ₄) ₃	e	8.2	7.0	b	10	10	10	6.7
Anionic 1	e	0.40	0.40	b	0.40	0.20	0.40	0.36
Al ₂ (SO ₄) ₃	e	7.1	7.0	b	10	9	9	6.8
Anionic 2	e	0.20	0.20	b	0.20	0.20	0.20	0.20
Al ₂ (SO ₄) ₃	5.4	0.4	5.0	b	7	10	10	6.8
Nonionic 2	0.40	0.40	0.40	b	0.40	0.20	0.40	0.367

^apH of supernatant immediately after sedimentation.

^bTrue color of water was =0.

^cIsoelectric point was not reached over dosage range tested.

^dCast floc had no effect on apparent color throughout the entire dosage range.

^eMore than one isoelectric point indicated.

The isoelectric point is one of the more recent innovations in the control of colloidal stability. The foundation of the concept of colloidal control through the measurement of electrophoretic mobility is unique as it is the only concept, in a broad spectra of tests, that has evolved from physical chemical theory. The focus of this paper, as previously stated, is to examine the practical relationship between two diverse methods of isoelectric point determination and then to compare the results obtained by these methods with the more classical methods of coagulant dosage control.

The colloidal titration technique offers possibilities as a method for isoelectric point location (References 14, 15, 16). It has some advantages over the electrophoretic mobility methods as it does not require as much expense either in equipment investment or in time to complete sample analysis; however, as all techniques it does have shortcomings. From these studies there are apparently two major problem areas:

1. If the water sample is high in natural color or coagulant color (ferric salts), the color change at the endpoint of the titration is difficult, if not impossible, to detect. This observation has been made previously by Kawamura (References 15, 16).
2. If a polymer is used either as a coagulant or a coagulant aid, the data indicates that in some cases it will interfere with the stoichiometric reaction yielding rather unpredictable results. Representative plots of these irregularities observed in this study are shown in Figures 1 and 2, while more normal plots are shown in Figures 3 and 4.

The irregularities identified above could be explained in many ways; however, because of the recessive nature in the slope of the curves, it is felt that the active groups on the polymer are undergoing secondary reactions with the colloids added for the test. More specifically, because MGC and PVSK are themselves polyelectrolytes, the polymers are exchanging functional groups at critical points during the titration. These exchanges seem to be proportional to the dosages available; hence, the assumption made by the test that all reactions proceed stoichiometrically to completion breaks down and therefore the test itself breaks down.

Another attribute of the colloidal titration technique worth noting is that the test, in a manner similar to the COD test, is self-analyzing through the use of a distilled water blank. By using relative titration volumes, it is necessary to assure the concentration of only one of the reagents. The color change at the end of the titration also merits some mention. As indicated by previous discussion, excessive color in the water can inhibit the detection of color change at the endpoint of the titration. This fact leaves open an excellent area for future study as the test would be far more valuable if the color contrast at the endpoint were less subtle.

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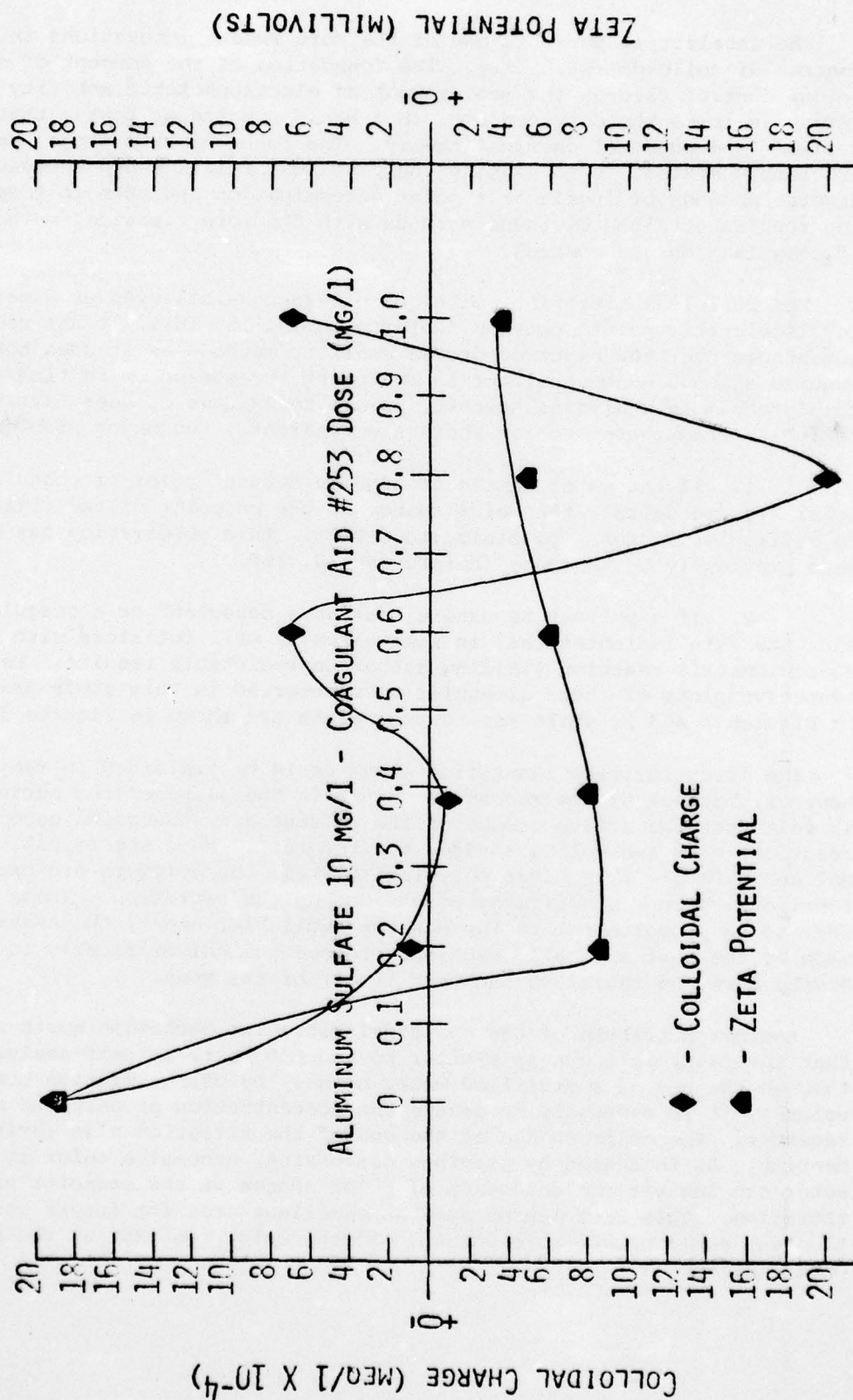


FIGURE 1
Electrophoretic Mobility as a Function of Aluminum Sulfate and Coagulant Aid 253 Dosage

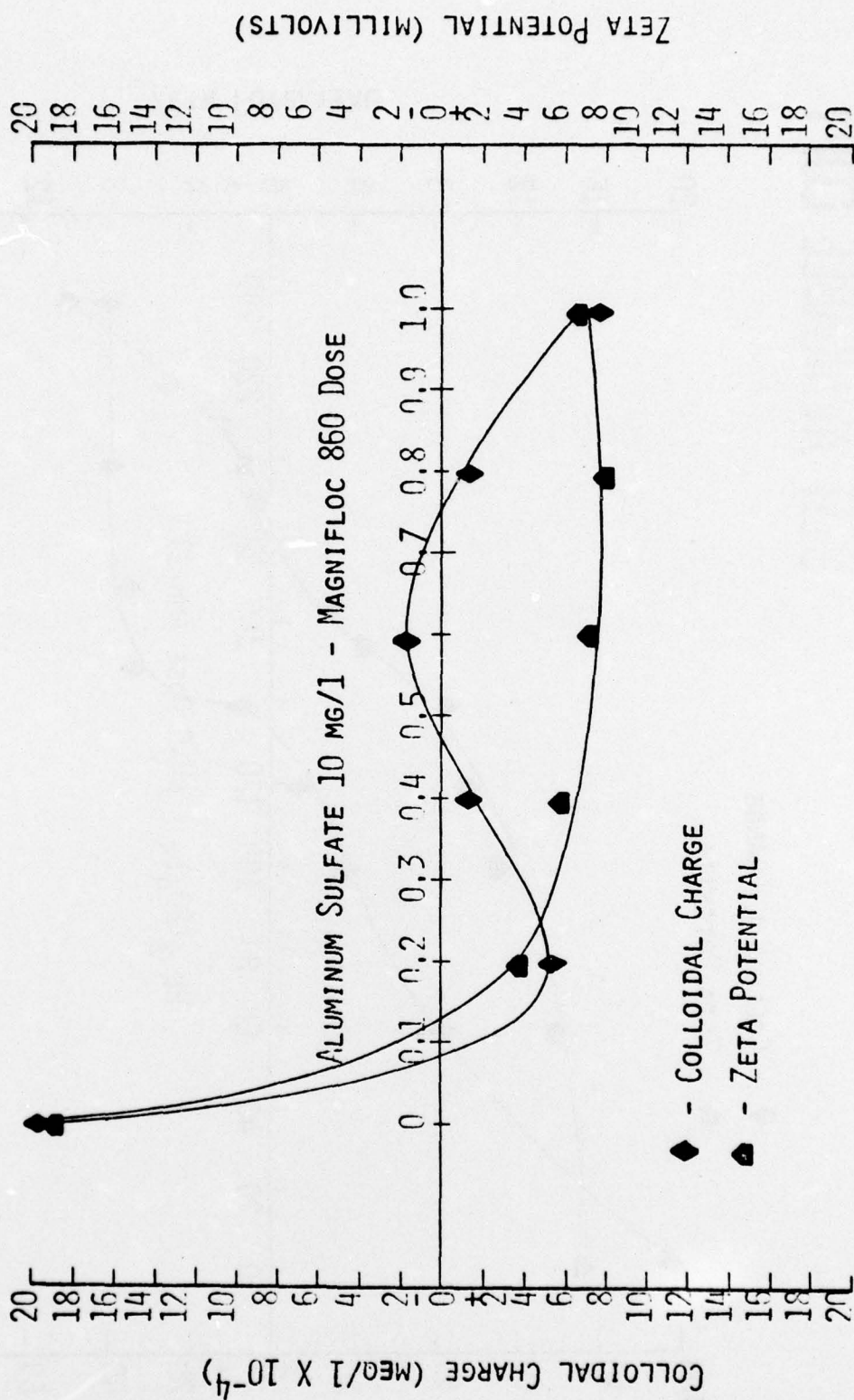


FIGURE 2
Electrophoretic Mobility as a Function of Aluminum Sulfate and Magnifloc 860 Dosage

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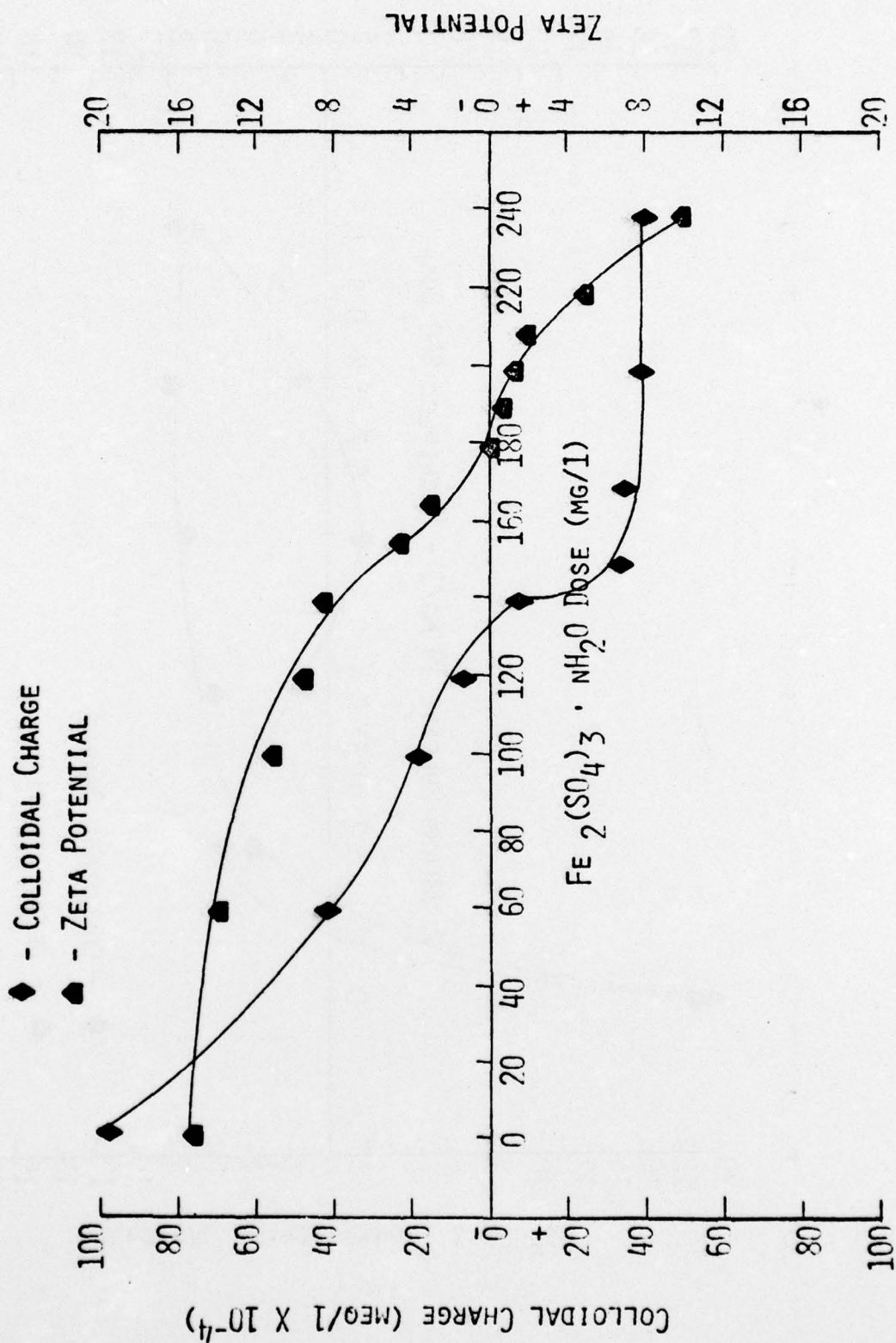


FIGURE 3
Electrophoretic Mobility as a Function of Ferric Sulfate Dosage

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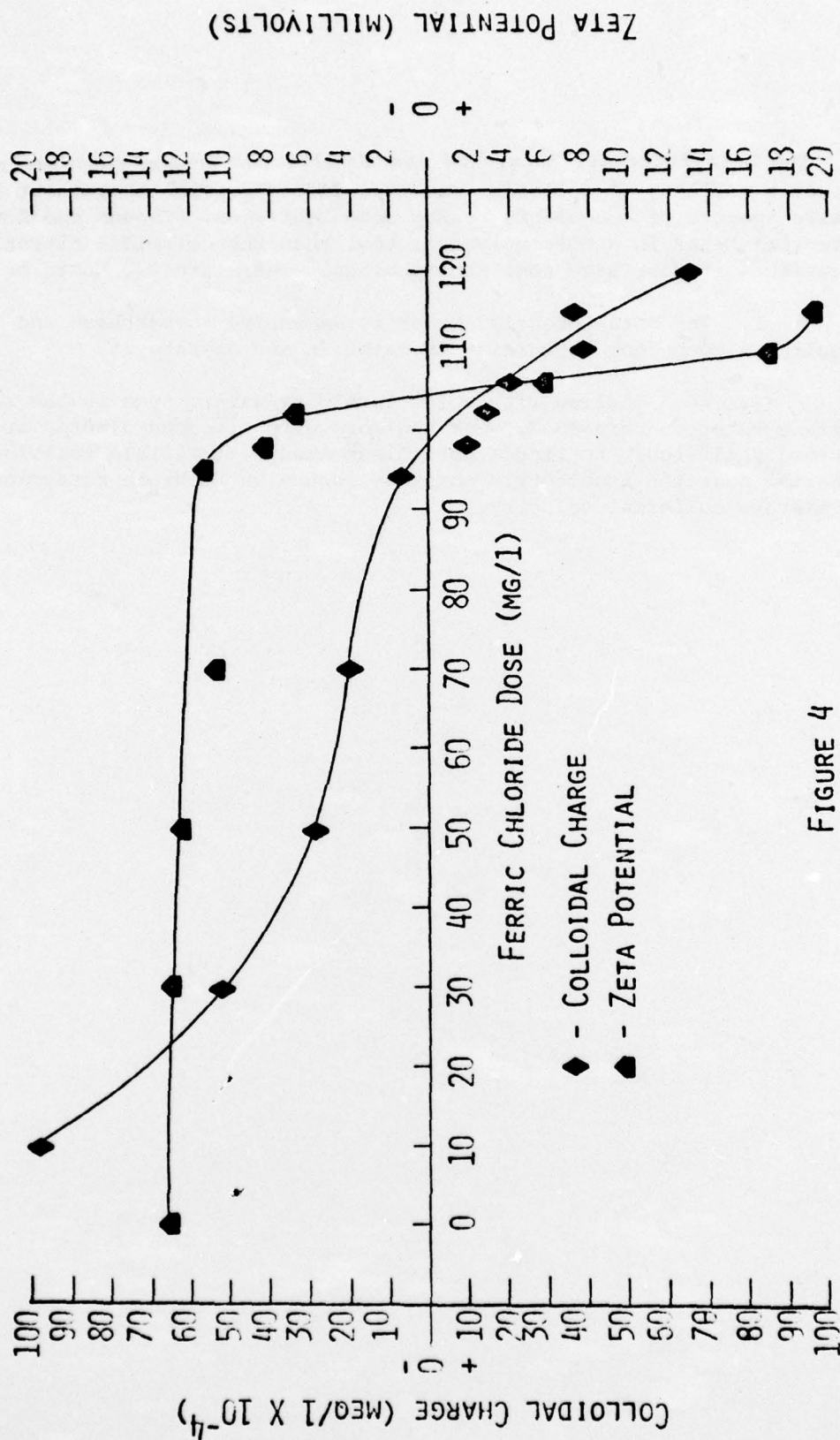


FIGURE 4

Electrophoretic Mobility as a Function of Ferric Chloride Dosage

The Zeta-Potential meter and its ability to measure the electrophoretic mobility of colloidal material offers promise throughout the entire spectra of coagulants and/or coagulant aids. Though the Zeta-Potential Meter is a more universal tool than the colloidal titration technique, it does have some shortcomings. There are two basic problems:

1. The Zeta-Potential Meter is expensive to purchase and requires a competent technician to maintain and operate it.
2. When dealing with a low turbidity water, such as the raw surface water in this study, and the more effective coagulants, it was extremely difficult to find a sufficient amount of visible colloidal material near the isoelectric point to insure an accurate determination of average colloidal velocity.

SECTION IV

CONCLUSION

1. The isoelectric point and its relationship to all parameters need further investigation. The colloidal titration technique and electrophoretic mobility methods for locating the isoelectric point do not always produce the same results (Figures 3 and 4); furthermore, the best coagulant dosage for physical and biological parameters does not correlate well with either method of isoelectric point location (Tables 3 and 4).

2. In the development of these isoelectric point systems for colloidal control, it has generally been assumed that the coagulant dosage for the best turbidity reduction parallels that dosage for the greatest bacteriological reduction. This is not necessarily the case as the facilities that remove turbidity are similar, but not the same as those that remove the biological fraction (particularly the bacteriophages). This can be seen by comparing the coagulant and/or coagulant aid dosages for bacteriophage, turbidity, and COD removal with the isoelectric point dosage as determined by both methods in Tables 3 and 4. Hence, turbidity and the isoelectric point should be viewed as approximate methods for the determination of coagulant dosages.

3. There is a critical need for further research to define just what is a "safe water" and what control tests should govern the admission of a water into the distribution system. The investigators feel that we cannot continue to produce water for human consumption relying upon antiquated standards, some of which have backgrounds so vague as to suggest nonexistence. The needed answers could become critical in the near future as the stresses upon our water environment continually increase.

REFERENCES

1. Adams, M. H., Bacteriophages, New York: Interscience Publishers, 1959.
2. Bean, E. L., "Study of Physical Factors Affecting Flocculation," Water Works Engineering 106:1:33, (January 1953).
3. Bean, E. L., Cambell, S. J., and Frederick, R. A., "Zeta Potential," Journal of the American Water Works Association (JAWWA) 56:21A, (Feb. 1964)
4. Behn, V. C., "Settling Behavior of Suspensions," Journal of the Sanitary Engineer Division, Proceedings of the American Society of Civil Engineers (JSED, ASCE), 83:paper 1423, (October 1957)
5. Black, A. P. and Hanna, S. A., "Electrophoretic Studies of Turbidity Removal by Coagulation with Aluminum Sulfate," JAWWA 53:438, 1961.
6. Bond, A. W., "Behavior of Suspensions," JSED, ASCE, 86, SA3 pp. 57-85, (May 1960)
7. Camp, T. R. and Stein, P. C., "Velocity Gradients and Internal Work in Fluid Motion," Journal Boston Society of Civil Engineers, 30:4:219 (October 1943).
8. Camp, T. R., "Flocculation and Flocculation Basins," Transactions of American Society of Civil Engineers (Trans. ASCE) 120:1 (1955)
9. Fair, G. M. and Geyer, J. C., Water Supply and Wastewater Disposal, pp. 634-639, Wily & Sons, New York, 1954.
10. Fitch, E. B., "Why Particles Separate in Sedimentation Processes," Industrial and Engineering Chemistry, 54:10:44 (October 1962)
11. Glasstone, S., A Textbook on Physical Chemistry, 2nd Ed. New York: D. Van Nostrand Company, Inc., 1946
12. Harrison, H. J., Kaufman, W. J., and Krone, R. B., "Orthokinetic Flocculation in Water Purification," JSED, ASCE, 92:SA6, pp. 95-111 (December 1966)
13. Hudson, H. E., "Physical Aspects of Flocculation," JAWWA, 57:895 (1965).
14. Kawamura, S. and Hanna, G. P., "Coagulant Dosage Control by Colloidal Titration Techniques," Purdue 21st Industrial Waste Conference: Part I, pp. 381 (May 1966).
15. Kawamura, S., "Removal of Color by Alum Coagulation - Part I" W & SW Jour., 114:282 (August 1967).

16. Kawamura, S., "Removal of Alum Coagulation - Part II" W & SW Jour., 114:324 (September 1967)
17. Langlierm, W. F., "Flocculation Phenomena - Turbid Water Clarification," Trans. ASCE, 188:147, (1953).
18. Mc Laughlin, R. T., "The Settling Properties of Suspensions," Journal of the Hydraulics Division, Transactions of the American Society of Civil Engineers, 85, HY12 (1959).
19. Marshall, C. Edmund, The Colloidal Chemistry of the Silicate Minerals. New York: Academic Press, Inc., 1949.
20. Riddick, T. M., "Role of Zeta Potential in Coagulation Involving Hydrous Oxides," TAPPI, 47-1:171A (January 1964).
21. Riddick, T. M., Control of Colloid Stability through Zeta Potential, Vol. 1. Wynnewood, Pennsylvania: Livingston Publishing Company, 1968
22. Sawyer, C. N. and McCarty, P. L., Chemistry for Sanitary Engineers. McGraw-Hill, New York, (1967)
23. Shelton, S. P. and Drewry, W. A., "Tests of Coagulants for the Reduction of Viruses, Turbidity, and Chemical Oxygen Demand" Journal AWWA 65:10, pg 627, 1973.
24. Standard Methods Water and Waste Water, 13th Ed. New York: American Public Health Association, 1971.
25. Stumm, W., Morgan, J. J., "Chemical Aspects of Coagulation." JAWWA, 54:971, (1962)
26. Stumm, W. and Morgan, J. J., Aquatic Chemistry, New York: Wily - Interscience, 1970
27. Thomas, A. W., Colloidal Chemistry. New York: McGraw-Hill, 1934
28. Yao, K. M., "Particle Aggregation in Water Pretreatment-Part I," W & SW Jour. 114:261, (July 1967).
29. Yao, K. M., "Particle Aggregation in Water Pretreatment-Part II," W & SW Jour. 114:295, (August 1967).
30. York, D. Y. and Drewry, W. A., Journal AWWA 66:711, December 1974
31. Zeta-Meter Manual. Second Edition. New York: Zeta Meter, Inc., 1968.

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